

MOLECULAR MACHINES: ROTATIONAL MOTION, MOLECULAR IMPELLERS, AND AN OPERATIONAL NANOVALVE

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Collaborators

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Prof. Fraser Stoddart

Support

National Science Foundation (DMR, CHE, EC-NSF, NIRT)

MACHINE

Def: a system consisting of
moving parts
solid support
accomplishes a specific objective

Nanomachines require nano power supplies

Outline

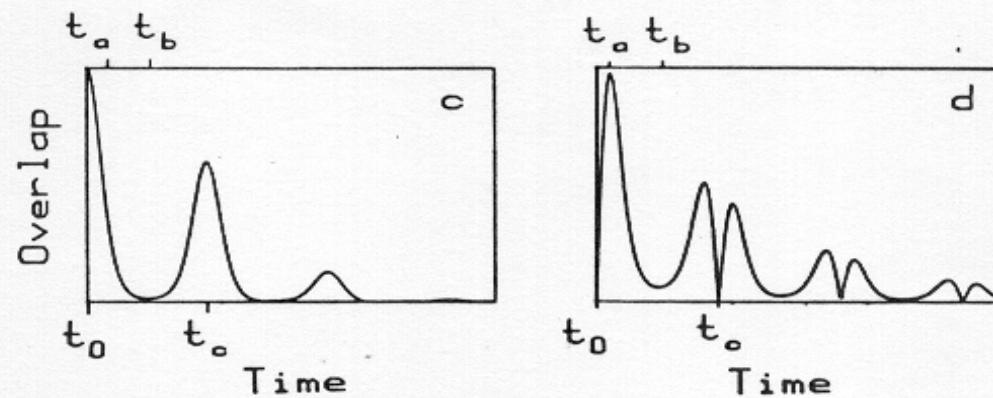
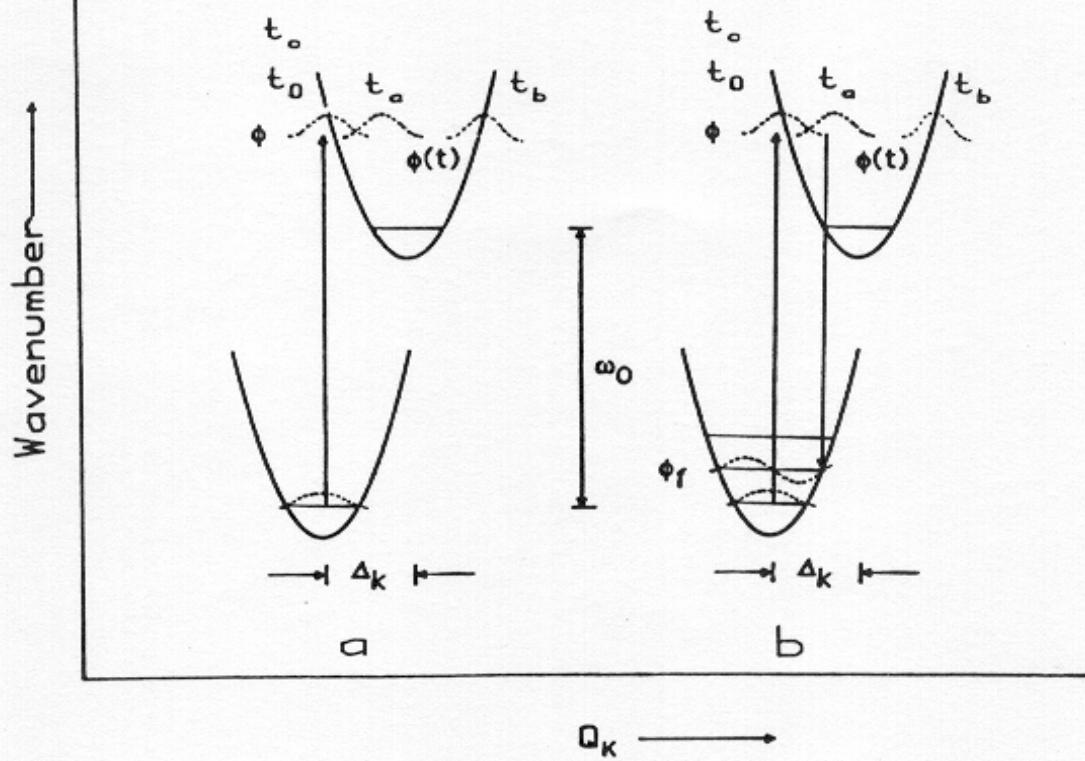
A. Introduction to Excited State Distortions

1. Time-dependent theory of electronic and resonance Raman spectroscopy -applications to excited state distortions
2. Simple application - metal-ligand bond lengthening
3. Advanced application - excited state mixed valence

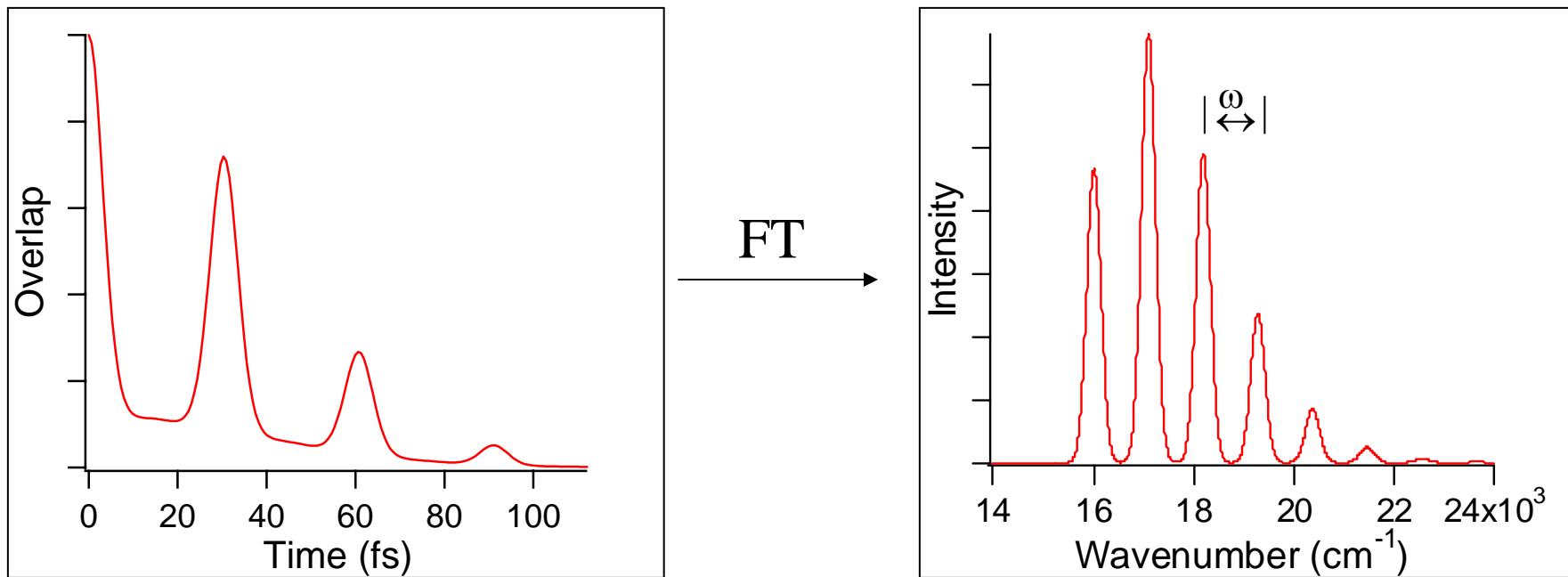
B. Molecular Machines

1. Nanostructured templated sol-gel films and powders
(the solid supports)
2. Deliberate placement of molecules
(the moving parts and the power supplies)
3. Nanomachines
(to accomplish the objectives of moving molecules through nanopores, and of trapping and releasing molecules)

Time Dependent View of Spectroscopy



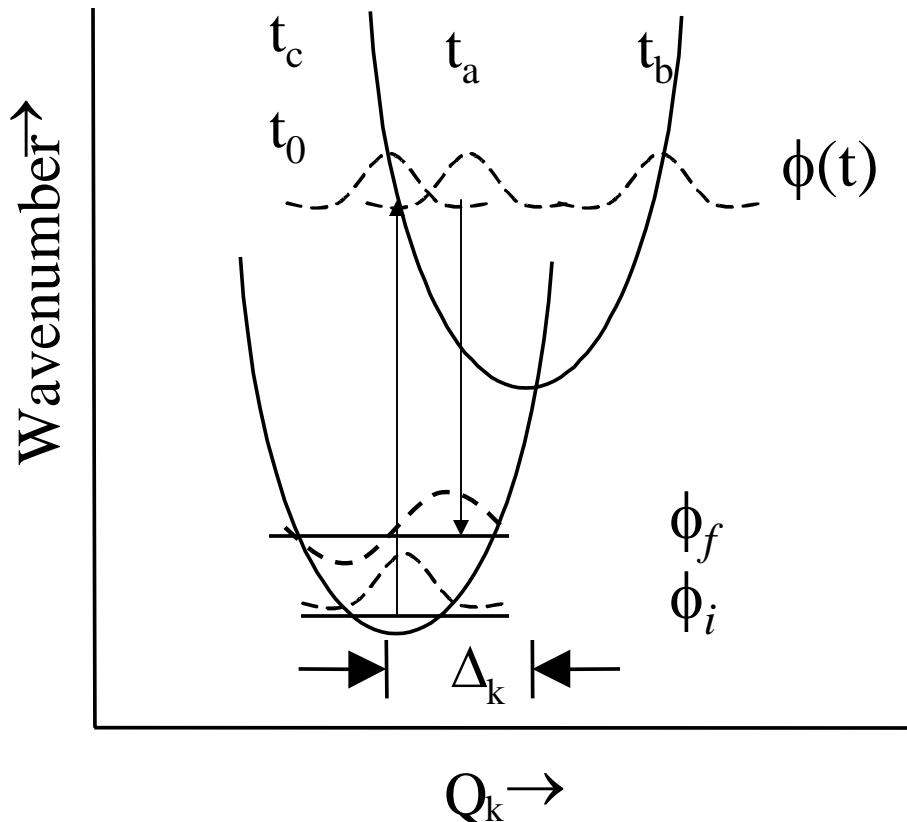
Calculated Absorption Spectrum



$$I(\omega) \propto \omega \int_{-\infty}^{\infty} e^{i\omega t} \langle \phi | \phi(t) \rangle dt$$

$$\langle \phi | \phi(t) \rangle = \prod_k \langle \phi_k | \phi_k(t) \rangle \exp(-iE_{00}t - \Gamma^2 t^2)$$

Time Dependent Theory of Resonance Raman Spectroscopy



- Eigenfunctions shown for the k^{th} symmetric mode
- Overlap of $\vec{x}(t)$ with \vec{x}_f is used to generate a resonance Raman profile
- Magnitude of ϕ determines relative intensity of mode

How To Determine Distortions

Measure absorption and emission spectra under conditions that produce the best-resolved vibronic structure

Measure resonance Raman excitation profiles

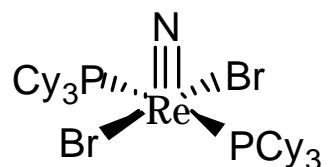
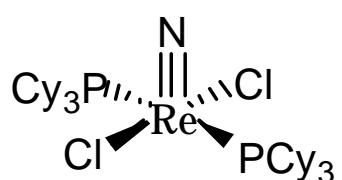
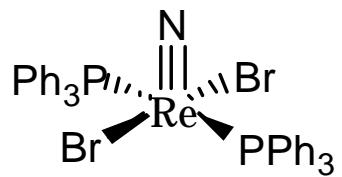
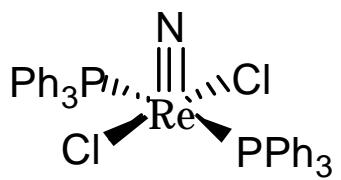
Use time-dependent theory, vary Δ until both electronic and Raman spectra are fit.

References:

A. Acosta, J. I. Zink, J. Organomet. Chem. **1998**, *554*, 87

K. S. Shin, J. I. Zink, Advances in Photochemistry, **1991**, *16*, 119

ONE VIBRATIONAL MODE AND ONE ELECTRONIC EXCITED STATE:



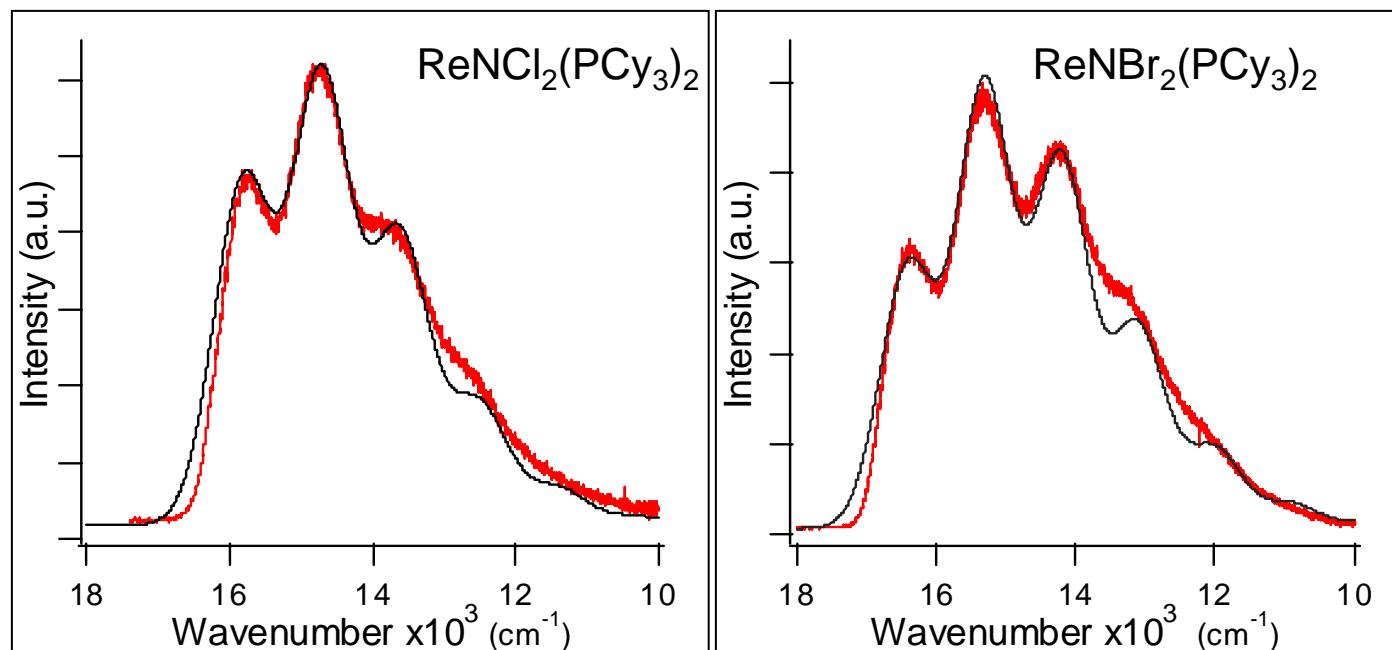
- Re(V) \equiv N compounds are known to luminesce and two six coordinate compounds have been reported with structure
- Five-coordinate, square pyramidal geometry is maintained by use of bulky phosphine groups
- A series of compounds was prepared to identify ligand modes that appear in the ReN stretching frequency range

Calculation of Structured Emission

Parameter	ReNCl ₂ (PCy ₃) ₂	ReNBr ₂ (PCy ₃) ₂	ReNCl ₂ (PPh ₃) ₂	ReNBr ₂ (PPh ₃) ₂
E _{oo} (cm ⁻¹)	15775	16375	15875	16300
ω (cm ⁻¹)	1100	1101	1095	1097
Γ (cm ⁻¹)	290	280	300	240
Δ	1.80	2.04	1.80	1.80

a. From emission spectra

b. From vibrational spectra

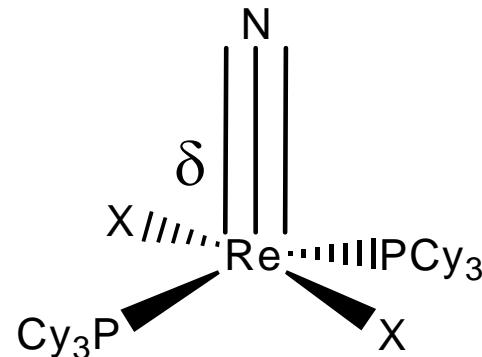


red lines, experimental

black lines, calculated

Calculation of Bond Length Changes

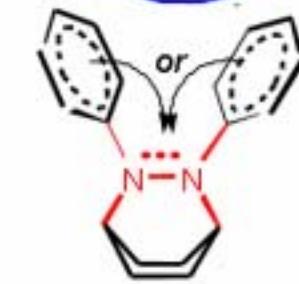
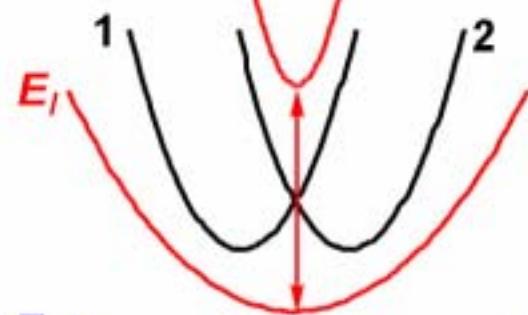
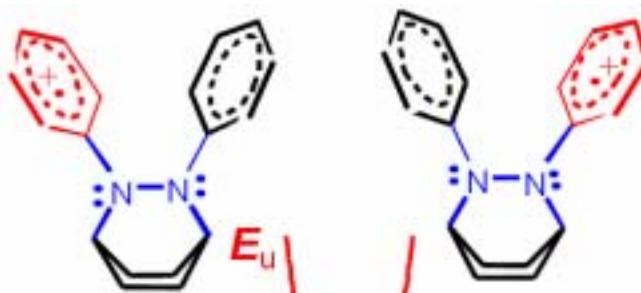
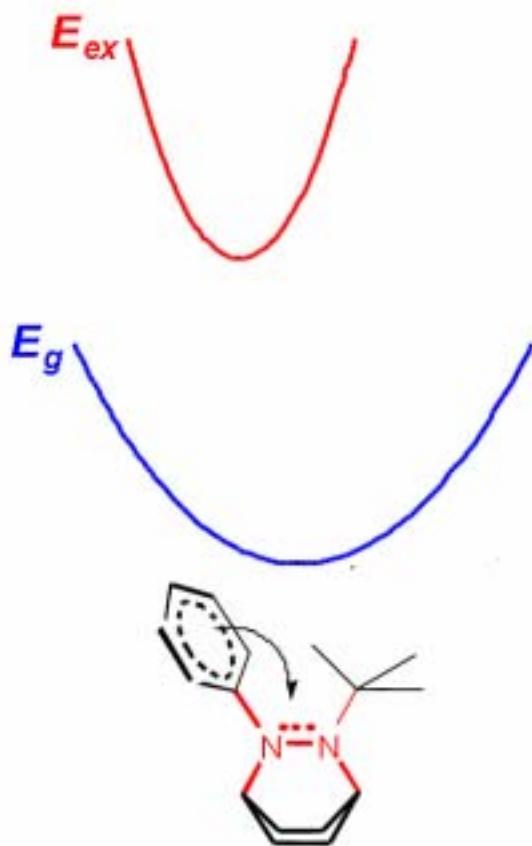
$\delta(\text{\AA})$	X =	$\text{PR}_3 =$
0.08	Cl	PCy_3
0.10	Br	PCy_3
0.80	Cl	PPh_3
0.80	Br	PPh_3

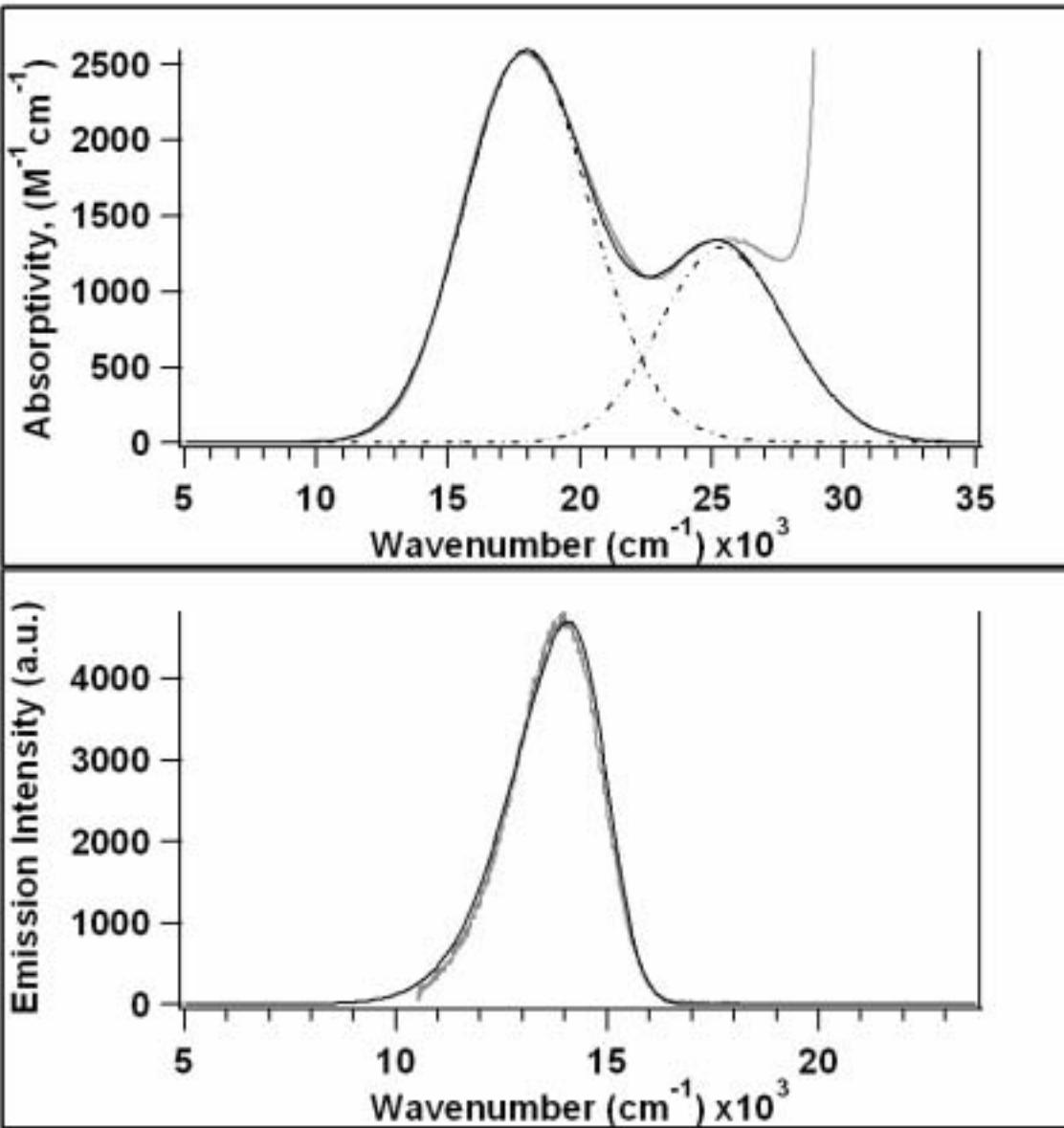


- Uncertainty in distortion is $\pm 10\%$
 - additional modes could change distortion
 - mass of vibration assumes N atom

S.E. Bailey, R.A. Eikey, M.M. Abu-Omar and J.I. Zink,

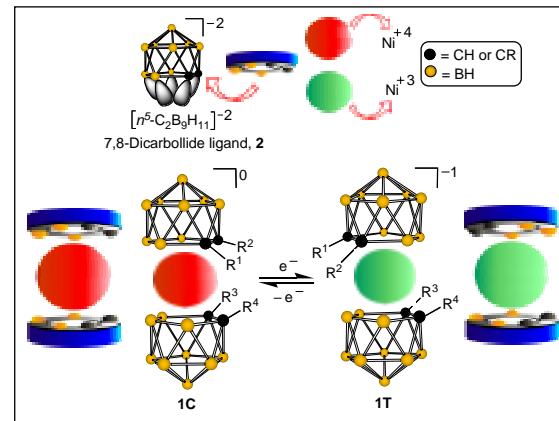
Inorg. Chem. **2002**, *41*, 1755



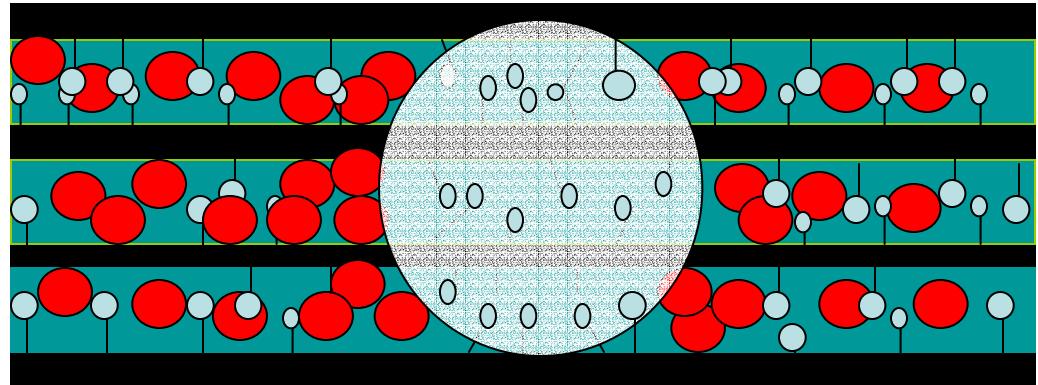


MOLECULAR MACHINES

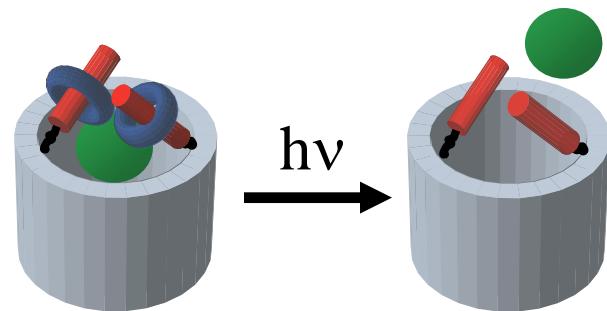
Rotational motion



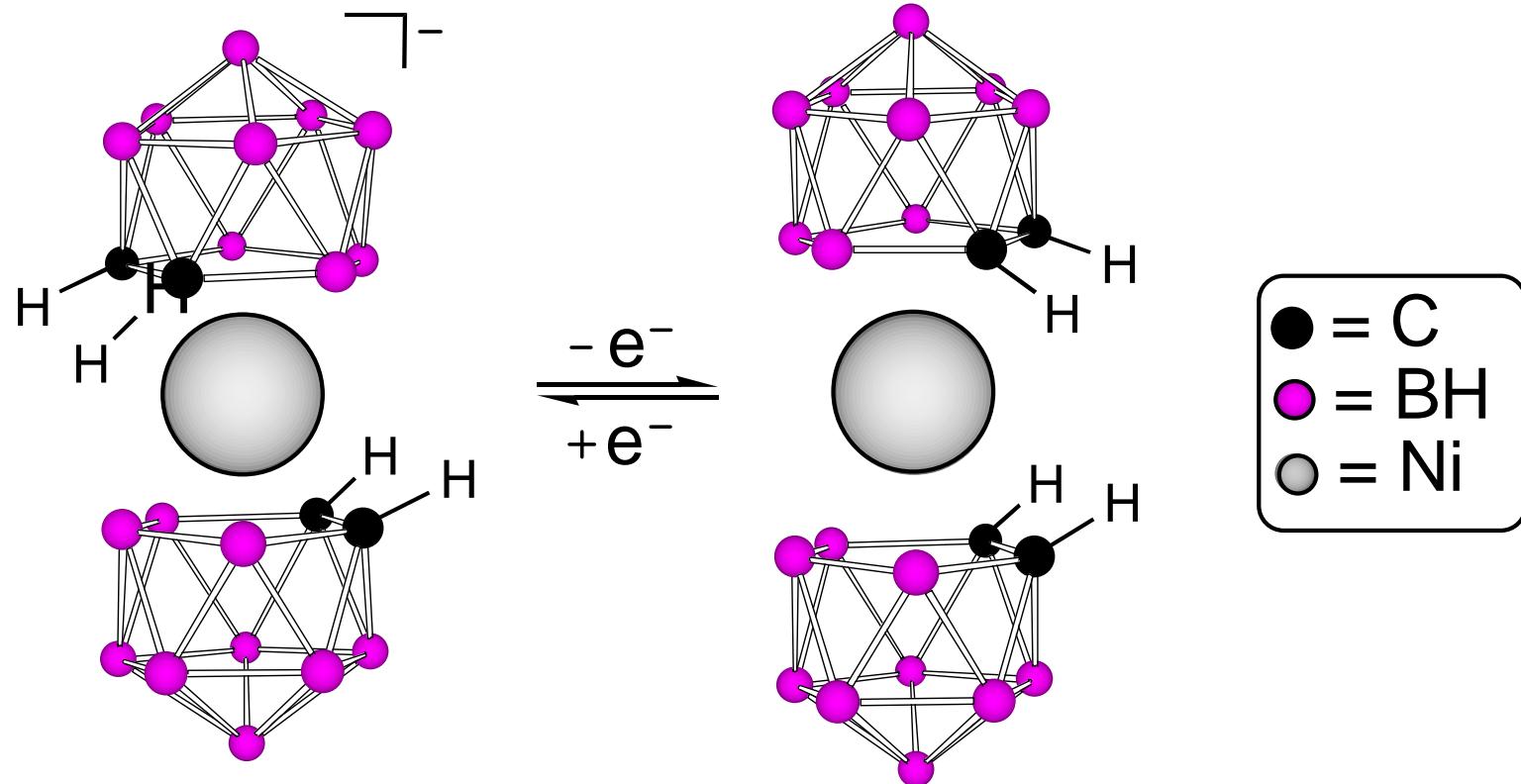
Moving
molecules through
pores



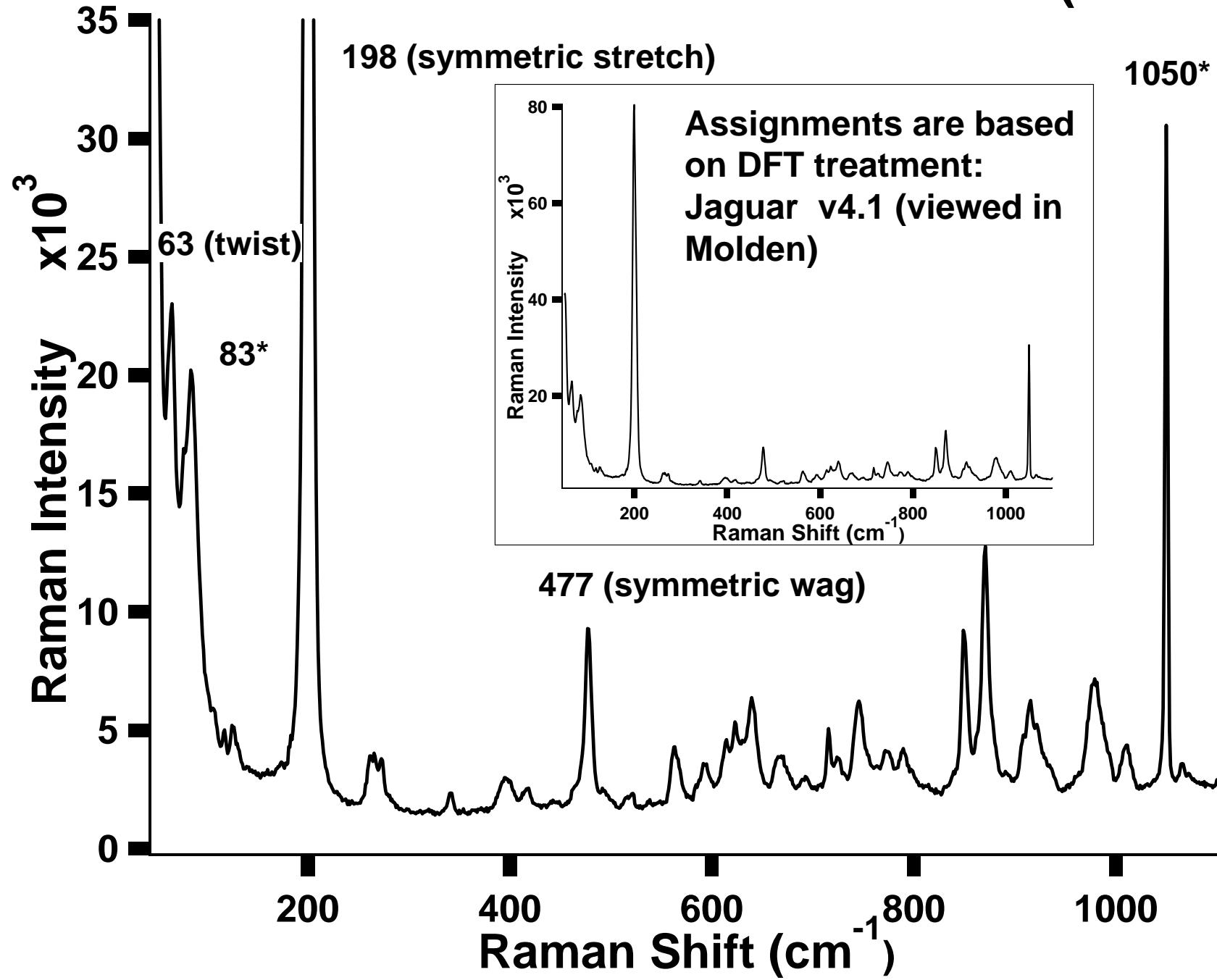
Nano valve

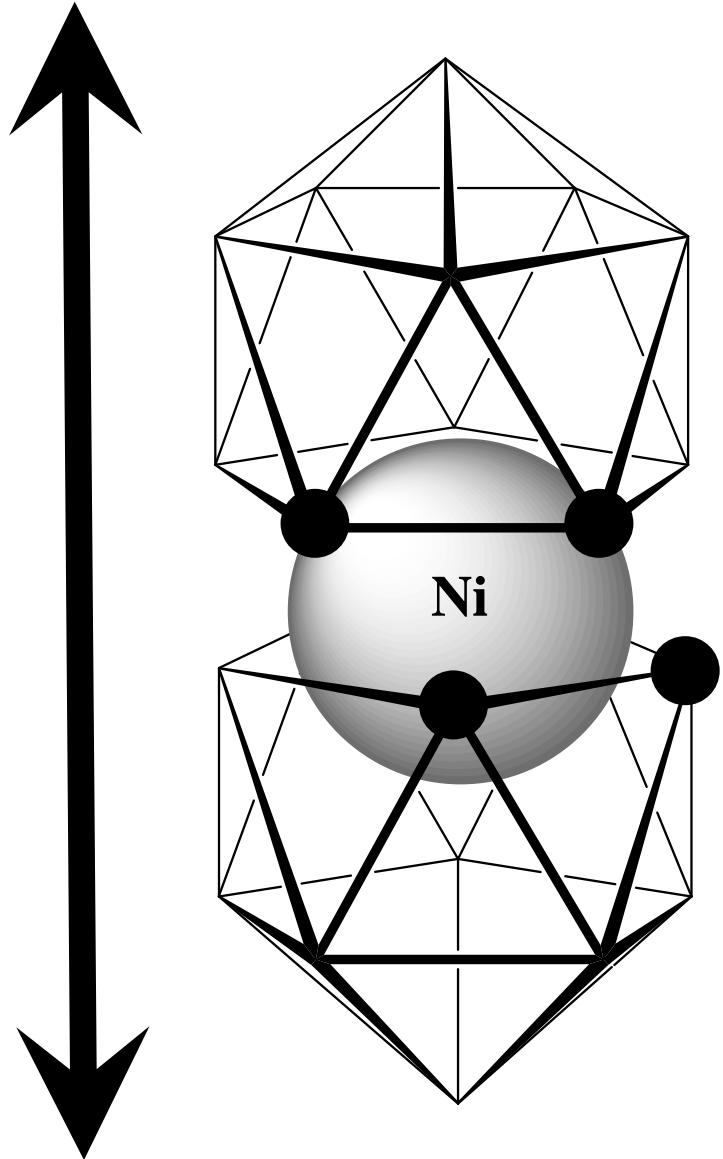


Rotary motion: metallacarboranes

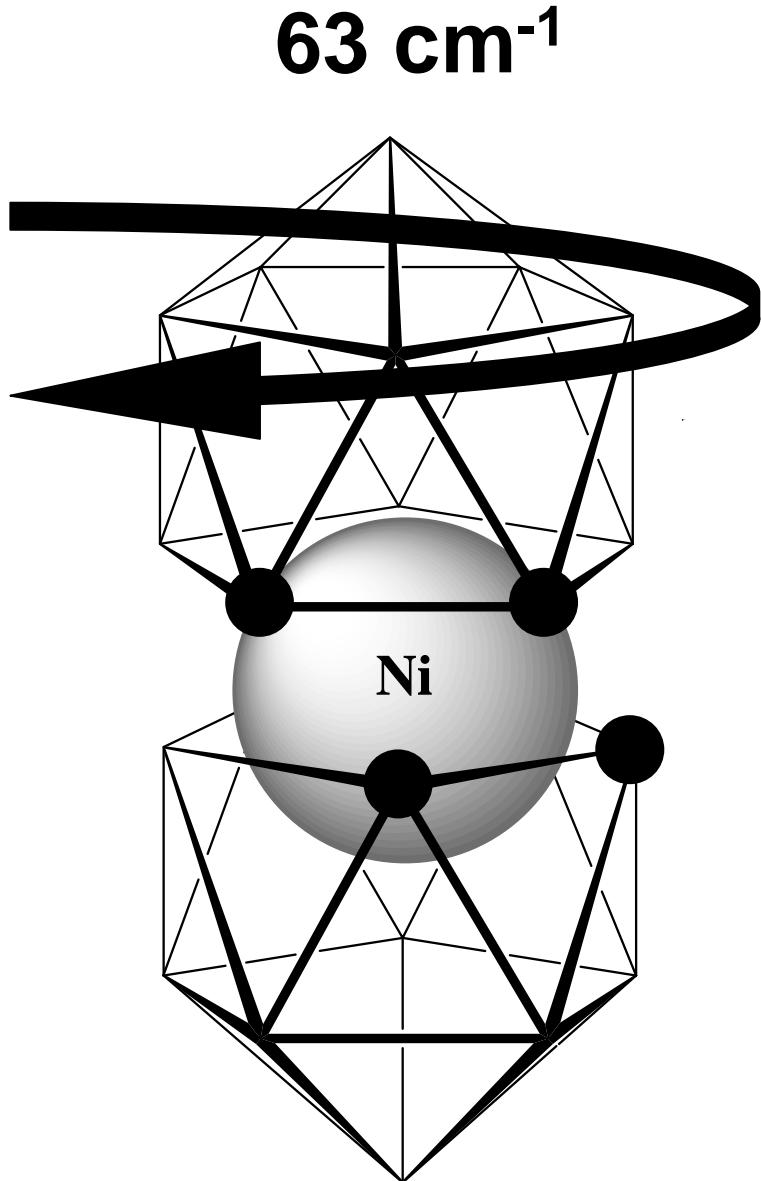


Resonance Raman (514.5 nm)

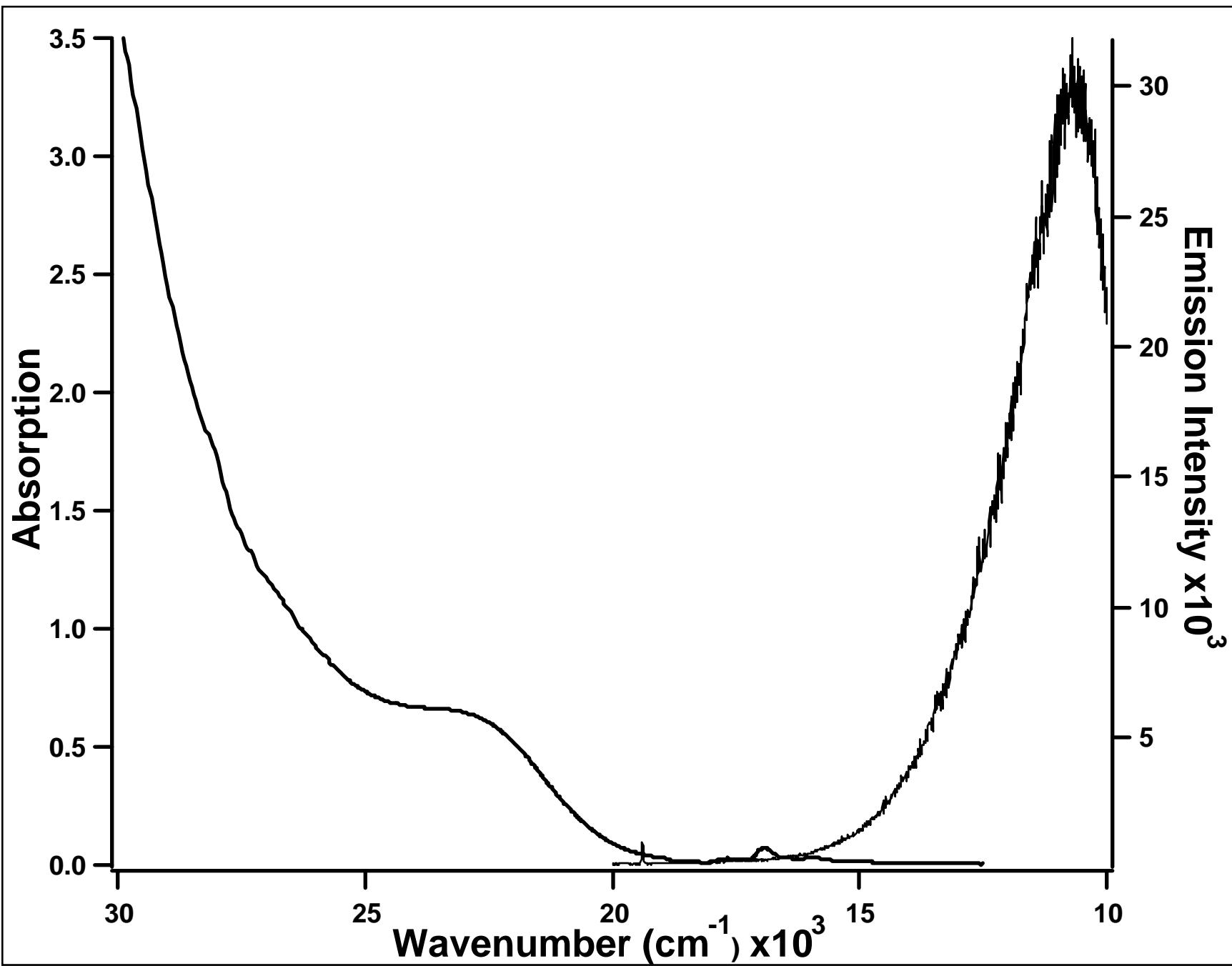


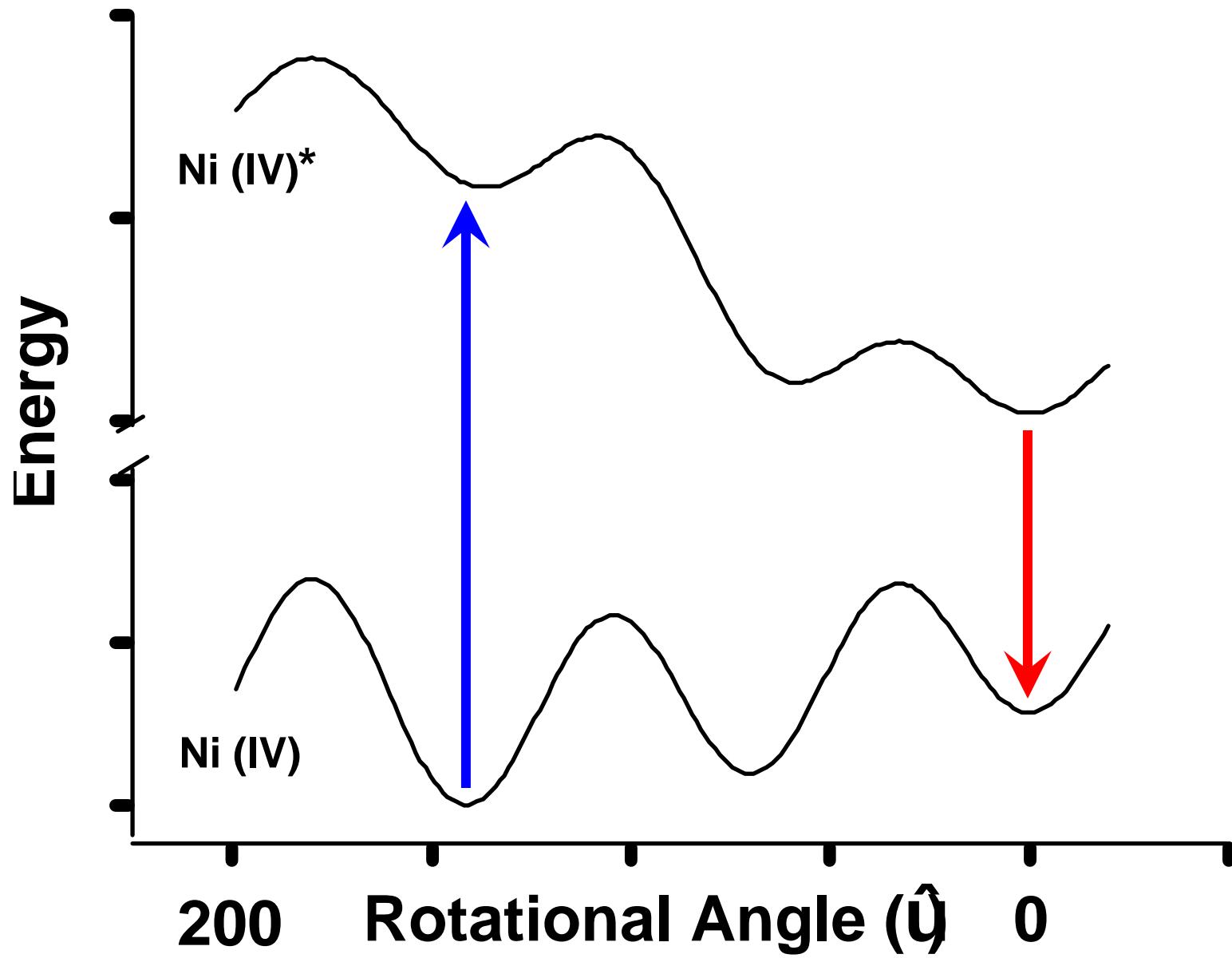


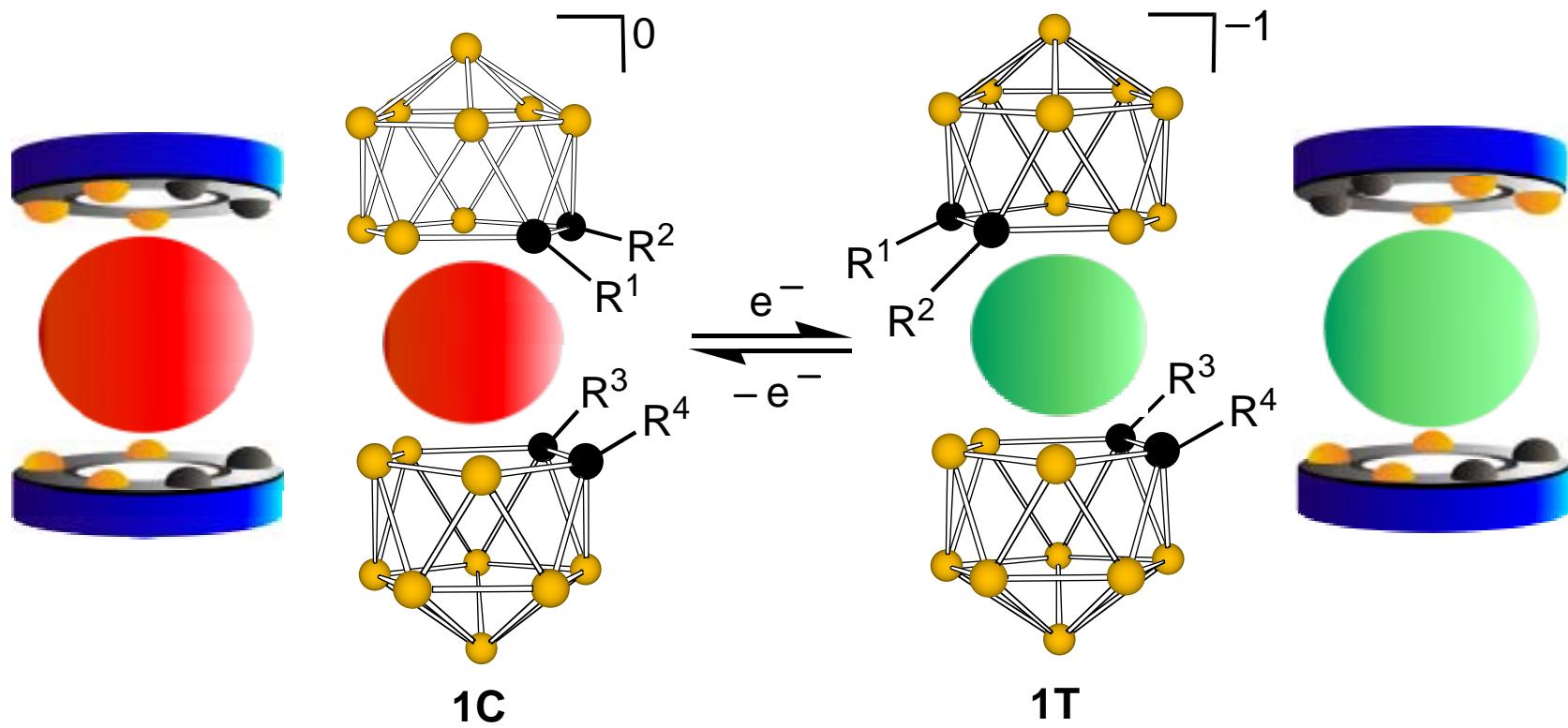
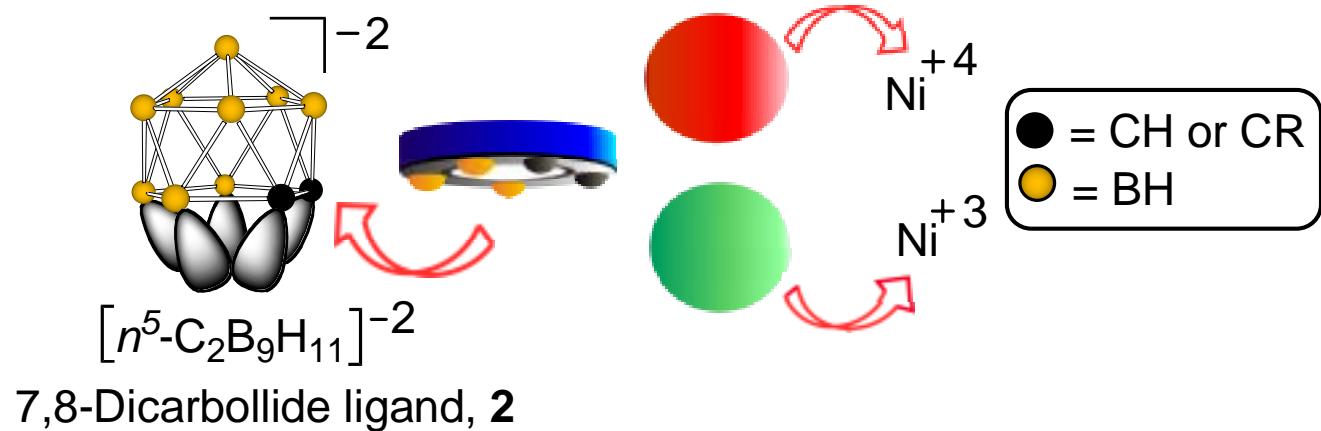
Symmetric L-M-L Stretch



Twist







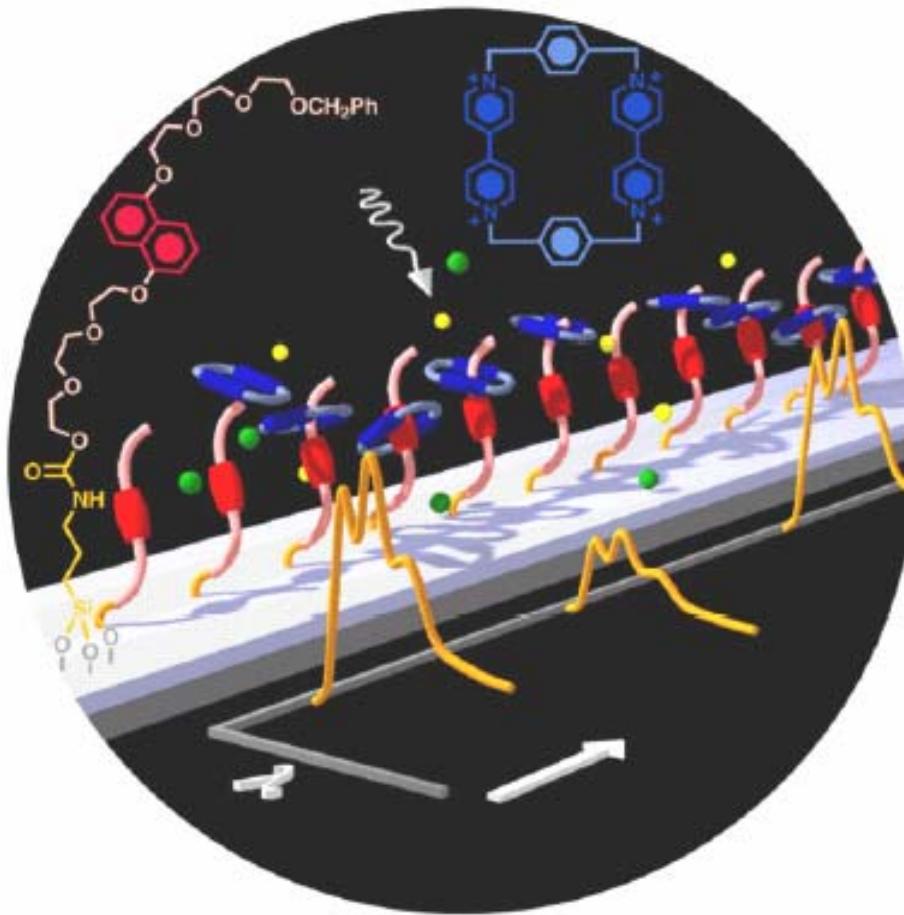
Summary

Rotating motor

Motion powered by electrical and light energy

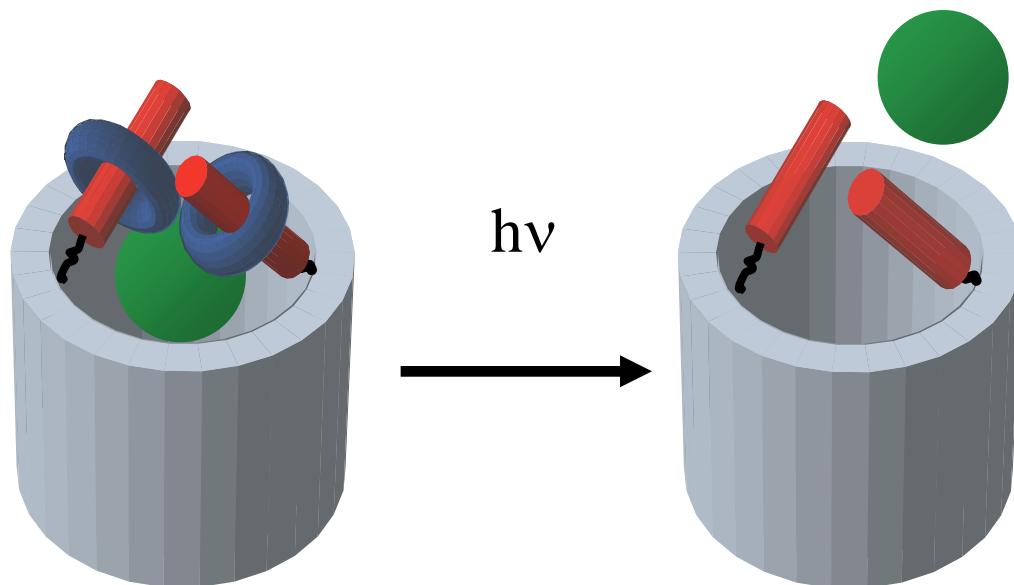
M. F. Hawthorne, J. I. Zink, J. M. Skelton, M. J. Bayer, C. Liu, E. Livshits, R. Baer, D. Neuhauser, *Science* 2004, **303**, 1849.

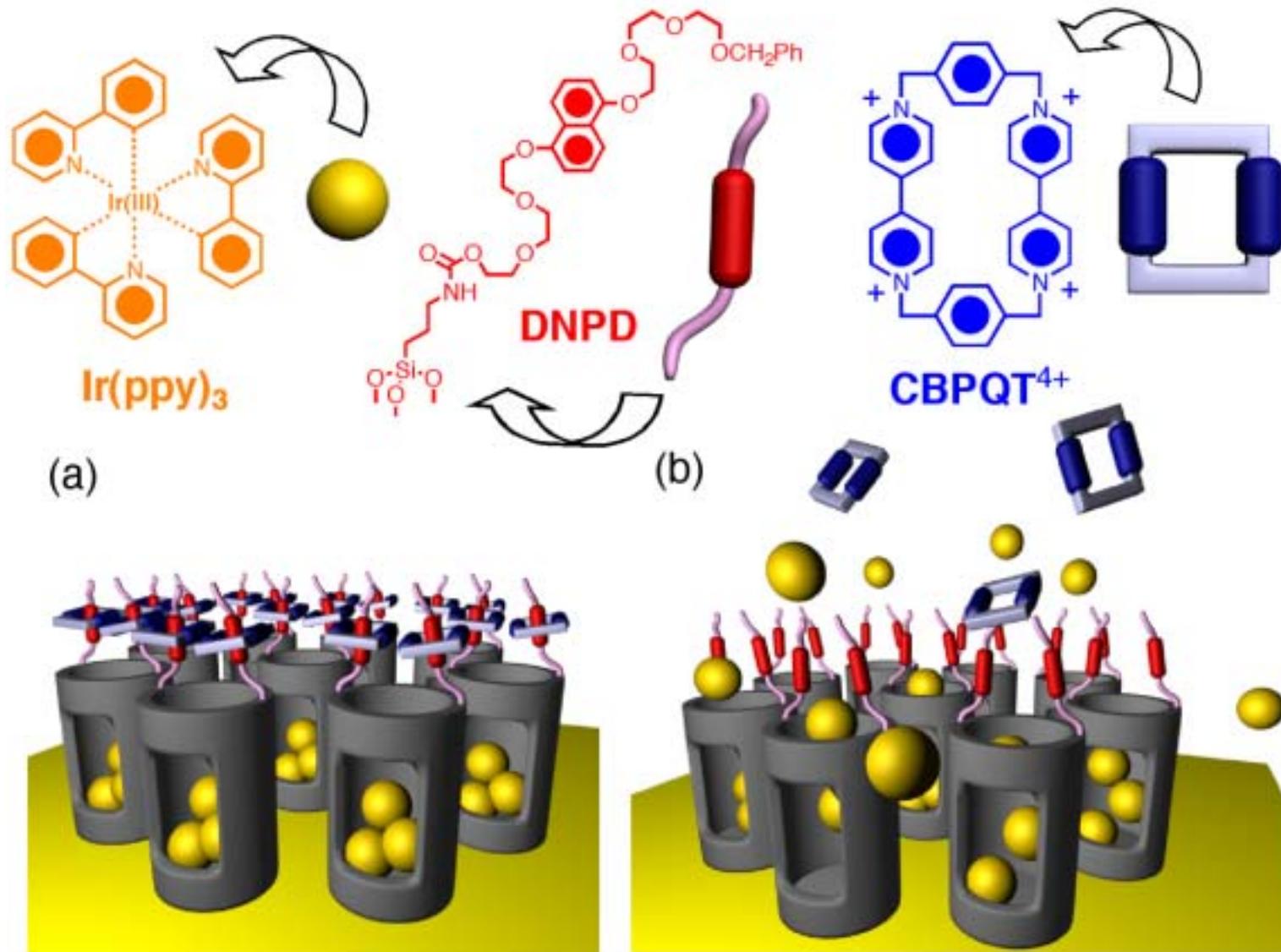
Nanovalve: pseudorotaxanes



Chia, Cao, Stoddart and Zink,
Angew. Chem. Int. Ed. 2001, 40, 2447.

Design of the Nanovalve





R. Hernandez, H.-R. Tseng, J. W. Wong, J. F. Stoddart, J. I. Zink,
J. Am. Chem. Soc. **126**, 3370 (2004).

Summary

- Nanostructured films and particles provide frameworks for molecular machines
- Active molecules are placed deliberately in specific spatially separated regions
- Rotational motion - metallacarboranes
- Oscillatory motion - azobenzenes
- Valve action - pseudorotaxanes

ACKNOWLEDGMENTS

Collaborators

Rotating Machine:

Prof. Fred Hawthorne, Dr. Michael Bayer, Prof. Danny Neuhauser, Prof. Roi Baer, Chris Liu

Azobenzene:

Prof. Luisa DeCola, Prof. Fritz Vögtle

Nanovalve:

Prof. Fraser Stoddart, Hsian-Rong Tseng, Jason Wong, Yi Liu, Amar Flood

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